

From Eqs. (1) and (2), the change in mass can be calculated as follows (Eq. 3):

$$\Delta m = -\frac{\Delta f}{Cf} \quad (3)$$

In [4], the authors compared the response of EQCM during the very early stages of the deposition of silver and copper on a gold substrate. Formation of copper ions as soluble intermediates during the deposition of copper causes a deviation of the frequency response from the expected one theoretically. Significant stress, which is observed only in the case of copper, is attributed to a large difference in the lattice parameter between gold and copper. During silver deposition, the frequency response follows the Sauerbrey equation, and no stress is observed.

The authors of [5–6] applied EQCM method when investigating copper electrodeposition. Anodic oxidation of copper electrodes in alkaline solutions was investigated using EQCM, CV, chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) measurements [5]. The participation of Cu^{3+} soluble species in the electrocatalytic oxidation of ethanol was proved by EQCM measurements, these data providing valuable information on the mechanism of the electrode process and formation of Cu^{2+} insoluble species from the reaction of Cu^{3+} with ethanol. Also, the results on the copper electrodeposition mechanism at different pH values were obtained using EQCM [6]. Direct reduction of Cu^{2+} and copper oxide (CuO) reduction at pH 2.0 and 4.5 occur simultaneously.

Activated carbon is a carbon-containing adsorbent having a large surface area and a developed porous structure. Activated carbon can be obtained from carbon-containing raw materials (rice husk, apricot stones, walnut shells, etc.) by physical and chemical activation methods [7–10]. According to the literature review, there are many works on using carbon adsorbents for adsorption of metals (Au^{3+} , Cr^{6+} , As^{3+} and others) and metal compounds [11–17]. However, only a few publications on the use of EQCM method for the study of Au^{3+} ions on the activated carbon adsorbents can be found in the literature.

In this study, we focused on the electrochemical quartz crystal microbalance method. This article reports on a study of Au^{3+} ions adsorption on activated carbon and gold electrodes for comparison by a combined electrochemical quartz crystal microbalance-cyclic voltammetry (EQCM-CV)

method. The frequency change during the adsorption of Au^{3+} ions was determined by EQCM simultaneously measuring the electrical charge in the electrochemical experiments.

2. Experimental

The resonant frequency of quartz crystal and electrochemical experiments were monitored by Autolab Potentiostat/Galvanostat Model AUT83945 (PGSTAT302N). The detection of chloroauric solution (HAuCl_4) was carried out by EQCM-CV analysis. The EQCM-CV studies were conducted in a three electrode cell with quartz plate coated with activated carbon and gold electrode the active surface of which was 0.361 cm^2 , gold wire (Au) as a counter electrode, and saturated Ag/AgCl in $3 \text{ mol}\cdot\text{L}^{-1}$ KCl as a reference electrode. A working solution with the concentration of $100 \text{ mg}\cdot\text{L}^{-1}$ was prepared by diluting the contents of the ampoules of the state standard sample of Au^{3+} ions (company «IRGIREDMET», Russia) with distilled water. The basic background electrolyte was a solution of $0.1 \text{ mol}\cdot\text{L}^{-1}$ hydrochloric acid.

The working electrode was made by coating a quartz plate with activated carbon from rice husk. Carbon coating consists of 85 wt.% activated carbon, 10 wt.% polyvinylidene fluoride (PVDF) from Sigma-Aldrich and 5 wt.% carbon black (C-65, Timcal C-NERGY Imerys). A detailed description of the procedure for producing activated carbon is given in [18]. The morphology of activated carbon after sorption of gold ions was determined by scanning electron microscopy (SEM, Quanta 3D 200i Dual System, FEI). The surface area of activated carbon was investigated on the analyzer «Sorbometr M» by low-temperature nitrogen adsorption using the method of Brunauer-Emmett-Teller (BET-method). As shown previously [18], the obtained carbon material from rice husk has a specific surface area of $2900 \text{ m}^2\cdot\text{g}^{-1}$.

3. Results and Discussion

3.1. Electroreduction of Gold on a Gold Electrode

The carbonized and activated rice husk (CARH) has a rather low redox potential and the stationary potential is 0.05 V (Ag/AgCl). The measured stationary (real) potential of $[\text{AuCl}_4^-]$ in a hydrochloric acid medium is equal to 0.47 V (Ag/AgCl). The potential difference between gold (oxidizing agent) and the sorbent (reducing agent) is 0.42 V relative to the reference.